Oxidation Reaction of $[\{Cu(Hpz)_2Cl\}_2]$(Hpz = pyrazole): Synthesis of the Trinuclear Copper(II) Hydroxo Complexes $[Cu_3(OH)(pz)_3(Hpz)_2Cl_2]$·solv (solv = H_2O or Tetrahydrofuran). Formation, Magnetic Properties, and *X*-Ray Crystal Structure of $[Cu_3(OH)(pz)_3(py)_2Cl_2]$·py (py = pyridine)*

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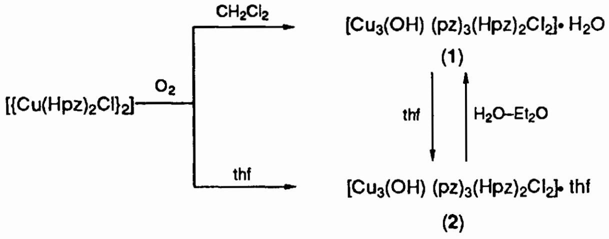
The trinuclear copper(II) complexes $[Cu_3(OH)(pz)_3(Hpz)_2Cl_2]$·solv (Hpz = pyrazole, pz = pyrazolate anion, solv = H_2O or tetrahydrofuran) have been obtained by oxidation reactions of $[\{Cu(Hpz)_2Cl\}_2]$. When treated with pyridine(py), both Cu^{II} derivatives gave the related compound $[Cu_3(OH)(pz)_3(py)_2Cl_2]$·py, which has been characterized by a single-crystal *X*-ray structure analysis. Crystals are orthorhombic, space group *Pnma* (no. 62), a = 19.883(3), b = 15.063(3), c =9.495(2) Å, Z = 4, R = 0.035 and R' = 0.041 for 1 472 absorption corrected reflections having $I > 3\sigma(I)$.

From the oxidation reactions of copper(I) compounds in the presence of an appropriate ligand, dimeric hydroxo-bridged copper(II) complexes have been often obtained.[1,2] However, aerial oxidation of the ionic copper(I) complex $[Cu(Hpz)_2]NO_3$ (Hpz = pyrazole) leads to the formation of the unexpected μ_3-hydroxo derivative $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$,[3] whose crystal structure has been determined. Our recent studies have been devoted to the chemical behaviour of the dimeric chloro-bridged complex $[\{Cu(Hpz)_2Cl\}_2]$, whose *X*-ray structure and reactivity with carbon monoxide have already been described.[4] This paper deals with the oxidation reaction of $[\{Cu(Hpz)_2Cl\}_2]$ with molecular oxygen, from which trinuclear copper(II) complexes $[Cu_3(OH)(pz)_3(Hpz)_2Cl_2]$·solv [solv = H_2O or tetrahydrofuran (thf)] have been isolated. Their reaction with pyridine (py) allowed the formation of the related compound $[Cu_3(OH)(pz)_3(py)_2Cl_2]$·py and the magnetic properties and *X*-ray structure of this copper(II) complex are reported herein.

Results and Discussion

By treating the dimeric copper(I)–pyrazole complex $[\{Cu(Hpz)_2Cl\}_2]$[4] with molecular oxygen in CH_2Cl_2 or thf solution, at room temperature, the trinuclear copper(II) derivatives $[Cu_3(OH)(pz)_3(Hpz)_2Cl_2]$·solv [solv = H_2O (**1**) or thf (**2**)] have been obtained (Scheme). Complex (**2**) can also be obtained by stirring a suspension of (**1**) in thf, while (**1**) can be isolated when (**2**) is suspended in moist diethyl ether. Analytical and i.r. data are in agreement with the assigned formulations. The i.r. spectrum of (**1**) shows two bands above 3 000 cm^{-1} [at 3 450 and 3 240 (br) cm^{-1}]. These peaks appear at 2 560 and 2 440 cm^{-1} for the related deuteriated complex $[Cu_3(OD)(pz)_3(Dpz)_2Cl_2]\cdot D_2O$, obtained by treating $[\{Cu(Dpz)_2Cl\}_2]$ with dioxygen. We assign the 3 450 cm^{-1} absorption to ν(OH) of water. The value is below that of the free water molecule, due to the presence of hydrogen bonds. The broad band at 3 240 cm^{-1} is the result of overlap between ν(OH) of the hydroxo group and ν(NH) of the co-ordinated pyrazole. In fact, the i.r. spectrum of complex (**2**), which does not contain clathrate water of crystallization, shows only a broad band at 3 252 cm^{-1}.



Scheme.

Moreover, the i.r. spectra of complexes (**1**) and (**2**) show several peaks characteristic of pyrazole and its anion.[5] Both (**1**) and (**2**), when treated with pyridine, gave the related copper(II) complex $[Cu_3(OH)(pz)_3(py)_3Cl_2]$·py (**3**). The i.r. spectrum of (**3**) exhibits, above 3 000 cm^{-1}, the typical pattern due to hydrogen bonds originating from the interaction between μ_3-OH and the pyridine of crystallization, in agreement with the *X*-ray structure determination (see below). Moreover, in the 1 550—1 700 cm^{-1} region, two bands (1 607 and 1 593 cm^{-1}) are present which are assigned to the co-ordinated and free pyridine, respectively.

Description of the Structure of Complex (**3**).—The crystal data and relevant intensity collection parameters are reported in Table 1.

The crystal structure of $[Cu_3(OH)(pz)_3(py)_2Cl_2]$·py (**3**) consists of discrete $[Cu_3(OH)(pz)_3(py)_2Cl_2]$ molecules (ORTEP view in Figure 1) and pyridine molecules of crystallization, interacting *via* a hydrogen bond; both molecules are located on a crystallographic mirror plane containing the whole pyridine

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* μ-Chloro-1:2κ^2*Cl*-chloro-3κ*Cl*-μ_3-hydroxo-κ^3*O*-tri-μ-pyrazolato-1:2κN^1N^2; 1:3κ^2N^1:N^2; 2:3κ^2N^1:N^2-bis(pyridine)-1κ*N*,2κ*N′*-tri-copper(II)–pyridine (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Crystal data for compound (**3**)

Formula	$C_{24}H_{25}Cl_2Cu_3N_9O$
M	717.05
Crystal system	Orthorhombic
Space group	*Pnma* (no. 62)
a/Å	19.883(3)
b/Å	15.063(3)
c/Å	9.495(2)
U/Å^3	2 844(2)
Z	4
D_c/g cm^{-3}	1.675
μ(Mo-K_α)/cm^{-1}	24.55
F(000)	1 444
Min. transmission factor	0.92
Octants of reciprocal space explored	$-h, +k, +l$
2θ range/°	6—48
Scan mode	ω
Scan width/°	1.0 + 0.35tanθ
Number of collected reflections	2 552
Number of unique observed reflections, $I > 3\sigma(I)$	1 472
Number of variables	193
R, *R'*[a]	0.035, 0.041
Goodness-of-fit[b]	1.209
Max. peak in the final Fourier difference map/e Å^{-3}	0.329

[a] $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$, $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. [b] Goodness-of-fit $= [\Sigma w(F_o - k|F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$, where N_o, N_v = number of observations and number of variables, respectively.

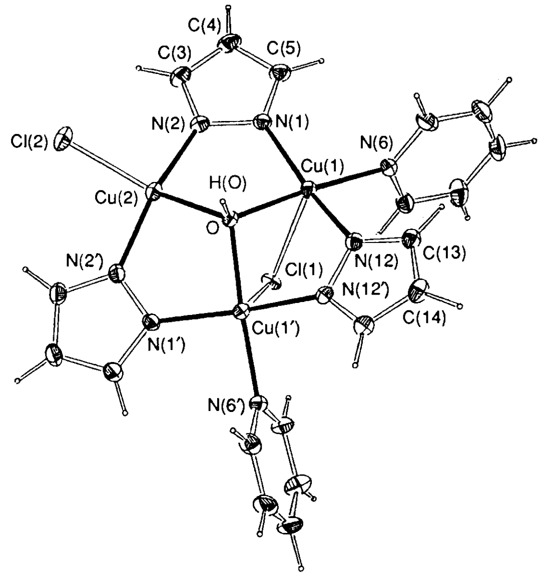

Figure 1. ORTEP drawing of the $[Cu_3(OH)(pz)_3(py)_2Cl_2]$ molecule, with partial atom labelling scheme. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms have been given, for sake of clarity, small thermal amplitudes

Table 2. Fractional atomic co-ordinates for compound (**3**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Cu(1)	0.098 69(3)	0.353 30(4)	0.046 66(7)
Cu(2)	0.017 19(5)	0.250	−0.210 9(1)
Cl(1)	0.187 1(1)	0.250	−0.089 9(2)
Cl(2)	−0.065 2(1)	0.250	−0.374 4(3)
O	0.041 4(2)	0.250	−0.009 0(5)
N(1)	0.065 4(2)	0.420 4(3)	−0.115 4(5)
N(2)	0.033 7(2)	0.376 9(3)	−0.221 7(5)
N(6)	0.163 0(2)	0.451 0(3)	0.105 7(5)
N(12)	0.107 0(2)	0.295 0(3)	0.231 2(4)
C(3)	0.019 9(3)	0.436 3(5)	−0.323 4(6)
C(4)	0.041 3(3)	0.518 2(5)	−0.284 2(7)
C(5)	0.070 1(3)	0.506 1(4)	−0.153 4(7)
C(7)	0.228 0(3)	0.441 4(4)	0.076 8(6)
C(8)	0.275 7(3)	0.502 3(5)	0.117 9(8)
C(9)	0.256 4(4)	0.574 3(5)	0.192 3(7)
C(10)	0.191 1(4)	0.585 8(4)	0.222 4(7)
C(11)	0.144 1(4)	0.523 7(4)	0.178 7(7)
C(13)	0.114 0(3)	0.322 8(4)	0.365 4(6)
C(14)	0.117 0(4)	0.250	0.453 2(9)
N(15)	0.081 0(3)	0.750	0.880 5(7)
C(16)	0.093 7(4)	0.750	0.744 3(9)
C(17)	0.156 6(4)	0.750	0.692 9(9)
C(18)	0.209 8(4)	0.750	0.783(1)
C(19)	0.198 1(4)	0.750	0.920(1)
C(20)	0.133 9(5)	0.750	0.962 4(9)
H(O)	0.0000	0.250	0.0273

Table 3. Relevant bond distances (Å) and angles (°) of compound (**3**) with e.s.d.s in parentheses *

Cu(1) ··· Cu(1′)	3.112(1)	N(1)–N(2)	1.359(6)
Cu(1) ··· Cu(2)	3.321(1)	N(2)–C(3)	1.346(7)
Cu(1)–Cl(1)	2.682(2)	C(3)–C(4)	1.357(9)
Cu(2)–Cl(2)	2.257(2)	C(4)–C(5)	1.381(8)
Cu(1)–O	2.000(3)	C(5)–N(1)	1.344(7)
Cu(2)–O	1.976(4)	N(6)–C(7)	1.330(7)
Cu(1)–N(1)	1.956(4)	C(7)–C(8)	1.376(8)
Cu(2)–N(2)	1.942(4)	C(8)–C(9)	1.351(10)
Cu(1)–N(6)	2.028(4)	C(9)–C(10)	1.342(10)
Cu(1)–N(12)	1.967(4)	C(10)–C(11)	1.385(10)
C(11)–N(6)	1.349(7)	N(12)–N(12′)	1.356(8)
N(12)–C(13)	1.349(6)	C(13)–C(14)	1.379(7)

Cu(2) ··· Cu(1) ··· Cu(1′)	62.06(1)	O–Cu(1)–N(1)	90.1(2)
Cu(1) ··· Cu(2) ··· Cu(1′)	55.88(1)	O–Cu(1)–N(6)	175.4(2)
Cu(1)–Cl(1)–Cu(1′)	70.93(5)	O–Cu(1)–N(12)	86.3(2)
Cu(1)–O–Cu(1′)	102.2(2)	O–Cu(1)–Cl(1)	78.1(1)
Cu(1)–O–Cu(2)	113.3(2)	N(1)–Cu(1)–N(6)	93.2(2)
Cl(2)–Cu(2)–O	147.5(2)	N(1)–Cu(1)–N(12)	163.7(2)
Cl(2)–Cu(2)–N(2)	95.0(1)	N(1)–Cu(1)–Cl(1)	98.1(1)
O–Cu(2)–N(2)	90.6(1)	N(6)–Cu(1)–N(12)	91.4(2)
N(2)–Cu(2)–N(2′)	159.6(3)	N(6)–Cu(1)–Cl(1)	98.2(1)

* Primed atoms are related by the $x, \frac{1}{2} - y, z$ symmetry operation.

and the Cl(2), Cu(2), O, H(O), Cl(1), and C(14) atoms of the trimetallic molecule.

Final atomic co-ordinates are reported in Table 2, while relevant bond distances and angles are collected in Table 3.

The $[Cu_3(OH)(pz)_3(py)_2Cl_2]$ molecule consists of a triangular arrangement of Cu^{II} atoms, connected by μ-pz ligands located slightly from the plane of the metal atoms (angles between pz ligands and Cu_3 plane: 13.1 and 27.7°). Three terminal ligands (one chlorine atom and two pyridine molecules), one on each copper atom, and two bridging ligands (one μ-Cl and one μ_3-OH) complete the co-ordination spheres of the three metal atoms (see Figure 1).

The non-bonding distances between adjacent Cu atoms [3.112(1) and 3.321(1) Å], which compare surprisingly well with those found in $[Cu_3(dppm)_3(OH)][BF_4]_2$[6] [dppm = bis(diphenylphosphino)methane] (although the latter possesses a different bridging system and Cu^I metal centres), however, do not exclude weak interactions, possibly mediated by the μ-pz ligands. A quantitative discussion of the spin coupling among the different copper atoms is given later.

Trimeric copper-pyrazolate complexes are not common, the only other Cu^{II} derivative structurally characterized being

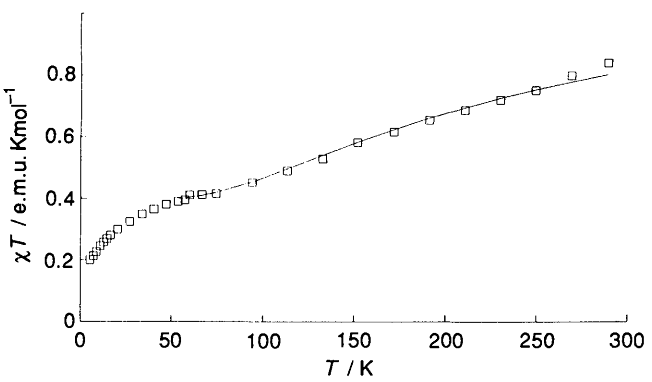

Figure 2. Plot of χT *vs.* T in the range 5—300 K. □, Experimental data; best fitting curve over the temperature range 50—300 K (see text); e.m. unit = S.I. × $10^6/4\pi$

$[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$.[3] The Cu–N and N–N distances of the nine-membered $\{Cu–N–N\}_3$ ring (average 1.957 and 1.356 Å, respectively) agree well with those found in $[\{Cu(OH)(pz)\}_8]$[7] and $[Cu_3(OH)(pz)_3(Hpz)_3(NO_3]_2]\cdot H_2O$,[3] although in the latter the Cu_3 system seems to be slightly expanded, with an average Cu–Cu distance of 3.345 Å. The terminally bound pyridines, with an average Cu–N bond length of 2.028(4) Å, are however only slightly more distant from the metal core in compound (**3**) than the terminal pyrazole ligands of $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$,[3] thus suggesting that steric effects in the apparently fairly crowded co-ordination sphere of Cu(1) are negligible. The terminal chlorine atom interacts with Cu(2), which shows a tetrahedrally distorted square-planar geometry, at a distance of 2.257(2) Å, which falls in the normal range (2.25—2.34 Å) for Cu^{II}–Cl bond lengths.[8] The bridging chlorine atom, however, at 2.682(2) Å from Cu(1) and with a Cu(1)–Cl(1)–Cu(1′) angle of 70.93(5)° is essentially separated from the adjacent copper atoms; normal symmetric Cu–Cl–Cu bridges in Cu–Cl–Cu–N–N five-membered rings range from 2.13 Å for $\{[Cu_2LCl_4(H_2O)]\cdot H_2O$,[9] L = 3,6-bis(2′-pyridyl)pyridazine} to 2.57 Å for $[PPh_4][Cu_2\{H_2B(pz)_2\}_2(pz)_2Cl]$;[10] longer Cu–Cl distances of 2.60 and 2.70 Å have been observed in the case of a very asymmetric bridge in the distorted square-pyramidal complex $[Cu_2LCl_4]\cdot EtOH$ [L = 3,6-bis(2-pyridylthio)pyridazine].[11] Our results exclude, however, the presence of an intermolecular interaction between Cl(1) and adjacent moieties, in a fashion similar to that found for the NO_3^- groups of $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$,[3] all intermolecular Cu–Cl distances being longer than 6 Å. As a result, the co-ordination observed around the Cu(1) atoms is essentially square planar, with *trans* angles N(1)–Cu(1)–N(12) and O–Cu(1)–N(6) of 163.7(2) and 175.4(2)°, respectively, the metal atom lying *ca.* 0.08 Å out of the plane of the four ligands. The weakly bound chlorine atom (discussed above) completes the co-ordination sphere, generating an elongated square-pyramidal geometry.

The nature of the μ_3–OH ligand has been determined on the basis of: (*i*) the presence of a well defined peak in the final Fourier difference map, whatever cut on sinθ was applied on the observed data; (*ii*) the presence of absorption bands above 3 000 cm^{-1} in the i.r. spectrum (Nujol mull); (*iii*) the electroneutrality of the crystal, assuming that all the copper atoms were in the +2 oxidation state; and (*iv*) the refined Cu–O distances [1.976(4) and 2.000(3) Å] which, on the basis of the trend observed for $Cu_3–\mu_3–O(H)_x$ bond lengths ($x = 0$, 1.87;[12] $x = 0.5$, 1.93;[13] and $x = 1$, 1.96—2.01 Å[3,6,12,14—17]), agree well with the latter. From the (unrefined) position of the H(O) atom, the following parameters for a *localized* hydrogen bond between the trimeric molecule and the pyridine molecule of crystallization were derived: O–H(O) 0.89, H(O)···N(15) 1.83, O···N(15) 2.70 Å {to be compared with the $[O–H\cdots O]^{3-}$ distance, 2.4 Å, of the *tunnelling* hydrogen bond of $[Cu_9(OHO)(OH)_6L_9]$[12] (L = 2,2,6,6-tetramethylheptane-3,5-dionate)}, and O–H(O)···N(15) 174.5°.

The shortest intermolecular Cu···Cu distance (of about 5.98 Å) excludes, at least in principle, any interaction between the spins of two different molecules, although low-temperature magnetic susceptibility measurements seem to suggest a clear quenching of the uncoupled electrons below 50 K (see below); from the crystallographic data available, it is not possible to exclude the presence of crystal-to-crystal phase transitions at low temprature {as suggested, for example, for the dimeric species $[Cu_2L_2Cl_2]\cdot MeOH$ [HL = 8-(salicylideneamino)-quinoline[18]]}, although a close inspection of the crystal packing shows well separated trimers in the room-temperature unit cell.

Magnetic Measurements.—The room-temperature effective magnetic moment per trimeric unit of complex (**3**) ($\mu_{eff.}$ 2.59), clearly indicates antiferromagnetic coupling, since the value expected for uncorrelated spins would be at least 3. The effective magnetic moment is also temperature dependent as indicated in Figure 2 which shows a plot of χT *vs.* T.

The exchange Hamiltonian for an isosceles triangular arrangement of three metals has the form given in equation (1),[19]

$$\mathscr{H} = J[S(1)\cdot S(2) + S(1')\cdot S(2)] + J'\cdot S(1)\cdot S(1') \qquad (1)$$

where J refers to the interaction between the unique metal and the other two, and J' to the interaction between the two symmetry-related metal centres. For three copper atoms, the low-lying spin states are, in the case of antiferromagnetic coupling, a ground doublet state, an excited doublet state at $+J - J'$, and an excited quartet state at $+\frac{3}{2}J$. The magnetic behaviour is therefore expected to follow the Curie law at very low temperatures when only the ground doublet state is thermally populated. The experimental data can be fitted satisfactorily according to equation (1) in the range 50—290 K and the parameters obtained are $g = 2.17$, J[Cu(1)–Cu(2)] = J[Cu(1′)-Cu(2)] = 148(1) cm^{-1}, and J'[Cu(1)–Cu(1′)] = 23(6) cm^{-1}.

The fitting of the data with only one coupling parameter led to a very similar value of J (= 140 cm^{-1}) and to only a slightly poorer quality of the fitting. Indeed, as has already been observed,[20] in these calculations J' has a higher degree of uncertainty.

The magnetic behaviour below 50 K is more difficult to rationalize. The experimental observation that the magnetic moment drops below the value expected for one unpaired electron suggests that other kinds of antiferromagnetic interactions are operative. On the basis of the *X*-ray structure determined at room temperature (see above), inter-trimer interactions are not expected from the exceedingly long and unfavourable contacts between trimers. However, we cannot rule out the occurrence of one of the processes possibly affecting the magnetic behaviour through a temperature-induced change in the molecular or spin assembly (magnetic lattice dimensionality 'cross-overs', lattice-driven phase transitions, *etc.*). In principle, antisymmetric exchange might also yield magnetic moment values smaller than expected for one unpaired electron.[21]

The coupling parameters obtained from the fitting in the 'well behaved' temperature range are comparable with those reported for analogous trimers where a Cu_3O moiety is present (see, for instance, Table 4 and refs. therein). They are also in line with the observation that the magnetic coupling increases with the coplanarity of the co-ordination planes of the metal atoms. In the present instance the planes defined by N(1), N(6) N(12),

Table 4. Dihedral angles (°) between the least-squares planes defined by CuL_4 square-planar co-ordination in different Cu_3O systems

Compound[a]	Cu(1)–Cu(2)	Cu(1)–Cu(3)	Cu(3)–Cu(1)	J[b]	Ref.
$[\{Cu_3(O)L_3(ClO_4)\}_2]$[c]	27	20	14	2 000	12
$[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$	35	24	23	400	3
$[Cu_3(OH)(L')_3(ClO_4)]^+$	40	28	31	244	12
$[Cu_3(OH)(pz)_3(py)_2Cl_2]\cdot py$	54	27	27	140	This work
$[Cu_3(OH)(L'')_3]^{2+}$	80	82	87	24	16
$[Cu_3(OH)(L''')_3]^{2+}$	83	86	82	30	*d*

[a] HL = 3-(Phenylimino)butan-2-one oxime; HL′ = 2-(methylimino)-1,2-diphenylethan-1-one oxime, HL″ = 7 amino-4-methyl-5-azahept-3-en-2-one and HL‴ = 8-amino-4-methyl-5-azaoct-3-en-2-one. [b] The reported values of J from the literature have been modified according to the definition used in this paper [see equation (1)]. [c] In $[\{Cu_3(O)L_3(ClO_4)\}_2]$ the change of hybridization of the central oxygen atom from sp^3 to nearly sp^2 increases the amount of coupling. [d] M. Kriatkowski, E. Kriatkowki, A. Olechnowicz, D. M. Ho, and E. Deutsch, *Inorg. Chim. Acta*, 1988, **150**, 65.

O around Cu(1), N(1′), N(6′), N(12′), O around Cu(1′), and Cl(2), N(2), N(2′), O around Cu(2) show dihedral angles of 54, 27, and 27° with each other, the related J values being $+23$ and $+148$ cm^{-1}. Table 4 reports, for comparison, the literature data concerning the dependence of the magnetic parameters on the angle between the co-ordination planes of square-planar Cu^{II} atoms within a group of similar trimeric compounds. A value of $J = 140$ cm^{-1} was assumed for complex (**3**) in order to compare it directly with the others obtained by fitting the magnetic susceptibility data with only one parameter, although the symmetry of the molecule was not strictly three-fold.

Experimental

Starting Materials.—Solvents were purified and dried by standard methods. Pyrazole (Hpz) was used as obtained commercially. The compound $[\{Cu(Hpz)_2Cl\}_2]$ was prepared as reported elsewhere.[4]

Physical Methods.—Infrared spectra of the solid compounds were recorded on a Perkin-Elmer 781 spectrophotometer in Nujol mulls. Magnetic susceptibilities in the range 5—300 K were measured using a fully automated AZTEC DSM5 susceptometer equipped with an Oxford Instruments CF1200S continuous-flow cryostat and a Bruker B-E15 electromagnet. Diamagnetic corrections were estimated from Pascal's constants.

Synthesis of $[Cu_3(OH)(pz)_3(Hpz)_2Cl_2]\cdot H_2O$ (**1**).—To a suspension of $[\{Cu(Hpz)_2Cl\}_2]$[22] (0.25 mmol) in CH_2Cl_2 (10 cm^3) an excess of copper powder was added with stirring. After 30 min the blue suspension converted into a colourless solution. Excess of copper powder was removed by filtration under an inert atmosphere and the solution was maintained for 2 h under a dioxygen atmosphere. Complex (**1**) was obtained as a green insoluble product and recovered by filtration. It was washed with CH_2Cl_2 and diethyl ether and dried under vacuum (Found: C, 28.70; H, 2.95; Cl, 10.85; Cu, 29.80; N, 21.90; O, 5.00. Calc. for $C_{15}H_{20}Cl_2Cu_3N_{10}O_2$: C, 28.40; H, 3.15; Cl, 11.20; Cu, 30.05; N, 22.10; O, 5.05%).

Synthesis of $[Cu_3(OH)(pz)_3(Hpz)_2Cl_2]\cdot thf$ (**2**).—This compound was obtained as described for (**1**), but using tetrahydrofuran (thf) instead of dichloromethane as solvent. Complex (**2**) can also be prepared by stirring a suspension of (**1**) in thf for 30 min, while (**2**) can be converted into (**1**) by stirring a suspension in moist diethyl ether (Found: C, 33.05; H, 3.60; N, 20.50; O, 4.45. Calc. for $C_{19}H_{26}Cl_2Cu_3N_{10}O_2$: C, 33.15; H, 3.80; N, 20.65; O, 4.65%).

Synthesis of $[Cu_3(OH)(pz)_3(py)_2Cl_2]\cdot py$ (**3**).—Complex (**1**) or (**2**) (0.15 mmol) was suspended in thf-pyridine (1:1) (10 cm^3) and stirred for 2 h. The green product (**3**) was recovered by filtration, washed with thf, and dried *in vacuo*. The presence of free neutral pyrazole in the mother-liquor was confirmed. Crystals suitable for *X*-ray structure analysis were obtained by slow diffusion of a thf solution of (**2**) into thf-pyridine (1:1) (Found: C, 40.25; H, 3.45; N, 17.50; O, 2.35. Calc. for $C_{24}H_{25}Cl_2Cu_3N_9O$: C, 40.20; H, 3.50; N, 17.60; O, 2.25%).

Crystallography.—*X*-Ray intensity measurements. A green prismatic crystal of (**3**) of approximate dimensions 0.10 × 0.12 × 0.15 mm was mounted in an arbitrary orientation on a glass fibre which was then fixed onto a goniometer head. Diffraction data were collected at room temperature on an Enraf-Nonius four-circle CAD-4 automatic diffractometer, controlled by a PDP 11/73 computer, using Mo-K_α radiation ($\lambda = 0.710\,73$ Å) from a highly oriented graphite monochromator, with the generator operating at 55 kV and 26 mA. The Enraf-Nonius program SEARCH was used to obtain 25 accurately centred reflections having $9 < \theta < 11°$, which were then used in the program INDEX to obtain approximate cell dimensions. Least-squares fitting of the setting angles of these reflections gave accurate refined cell dimensions, their standard deviations and an orientation matrix for data collection. 2 552 Independent reflections were then collected by the ω-scan technique in the $6 < 2\theta < 48°$ range ($-h$, $+k$, $+l$ octant). The intensities of three standard reflections, monitored at 3 600 s intervals, showed no systematic decay. The raw intensity data were corrected for Lorentz-polarization effects (including the polarization of the crystal monochromator) and then for absorption but not for extinction. The empirical method developed by North *et al.*[23] was used with the aid of ψ scans ($\psi = 0$—360°, every 10°) of three reflections having χ values near 90°.

Determination and refinement of the structure. The positions of the two independent copper atoms were determined from a three-dimensional Patterson function. The co-ordinates of the remaining non-hydrogen atoms were located by successive least-squares refinements and Fourier difference maps. The hydrogen atom of the hydroxo group, H(O), was located but not refined, and given an isotropic thermal parameter of 7 Å^2. The same value was assigned to all other hydrogen atoms introduced in calculated positions (C–H 0.95 Å). Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Full-matrix least-squares refinement was based on F, the minimized function being $\Sigma w(|F_o| - k|F_c|)^2$. Weights were assigned as: $w = 1/\sigma^2(F_o)$, where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (pI)^2]^{\frac{1}{2}}/L_p$ where L_p is the Lorentz polarization factor, and p, the ignorance factor, set at 0.045. 1 472 Reflections with $I > 3\sigma(I)$ were used in the final refinement of the structural parameters. The atomic scattering factors, corrected for real and imaginary dispersion terms, were taken from ref. 24.

All computations were performed on a PDP 11/73 microcomputer using the SDP Plus package[25] and the physical constants tabulated therein.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Conclusion

Reaction of $[\{Cu(Hpz)_2Cl\}_2]$ with molecular dioxygen gives the trimeric compounds $[Cu_3(OH)(pz)_3L_2Cl_2]$·solv [L = Hpz, solv = H_2O (**1**) or thf (**2**); L = solv = py (**3**)], analogously to the reaction of $[Cu(Hpz)_2]NO_3$ with O_2.[3] For the pyridine substituted compound (**3**), however, the presence of chlorine ligands on Cu^{II} keeps the molecular units well separated in the room-temperature crystal lattice, and no mediated interactions between trimers are observed. It is noteworthy that from the analytical and structural data available for (**1**)—(**3**) (and also in $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]$·$H_2O$[3]) the hydroxo group of the $Cu_3(OH)(pz)_3$ unit is hydrogen bonded to solvent molecules of very different base strengths (pyridine, water or thf), thus preventing direct inter-trimer interactions.

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